

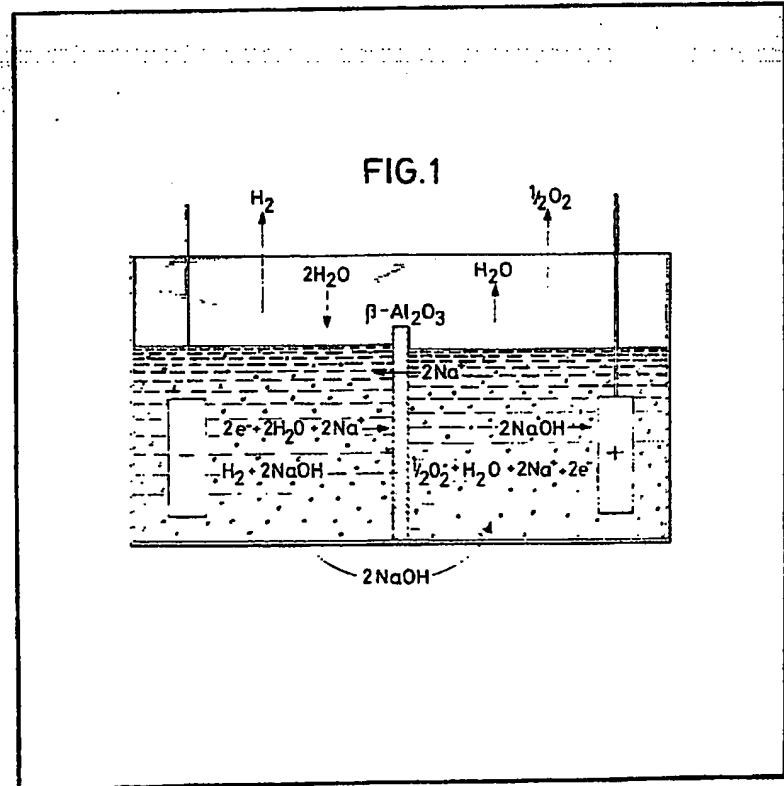
# UK Patent Application (19) GB (11) 2 010 333 A

(21) Application No 7848977  
(22) Date of filing 18 Dec 1978  
(23) Claims filed 18 Dec 1978  
(30) Priority data  
(31) 2756569  
(32) 19 Dec 1977  
(33) Fed. Rep. of Germany (DE)  
(43) Application published  
27 Jun 1978  
(51) INT CL<sup>2</sup>  
C25B 1/10  
(52) Domestic classification  
C7B 146 215 235 265  
268 329 402 503 508 511  
514 517 554 758 769 D8  
DN  
(56) Documents cited  
GB 1491905  
(58) Field of search  
C7B  
H1B  
(71) Applicant  
Kernforschungsanlage  
Jülich, Gesellschaft Mit  
Beschränkter Haftung,  
Postfach 1913, 5170  
Jülich, Germany  
(72) Inventors  
Jiri Divisek,  
Jürgen Mergel  
(74) Agent  
Mewburn Ellis & Co.

## (54) Process and Apparatus for the Production of Hydrogen and Oxygen

(57) In the electrolytic production of hydrogen and oxygen by electrolysis of molten alkali metal hydroxide, the

anode and cathode chambers are separated by means of a separator consisting of  $\beta$ -Al<sub>2</sub>O<sub>3</sub>, which provides effective separation of the anode and cathode chambers and can withstand the hot alkali melt. A Ni anode and Ni or graphite cathode may be used.

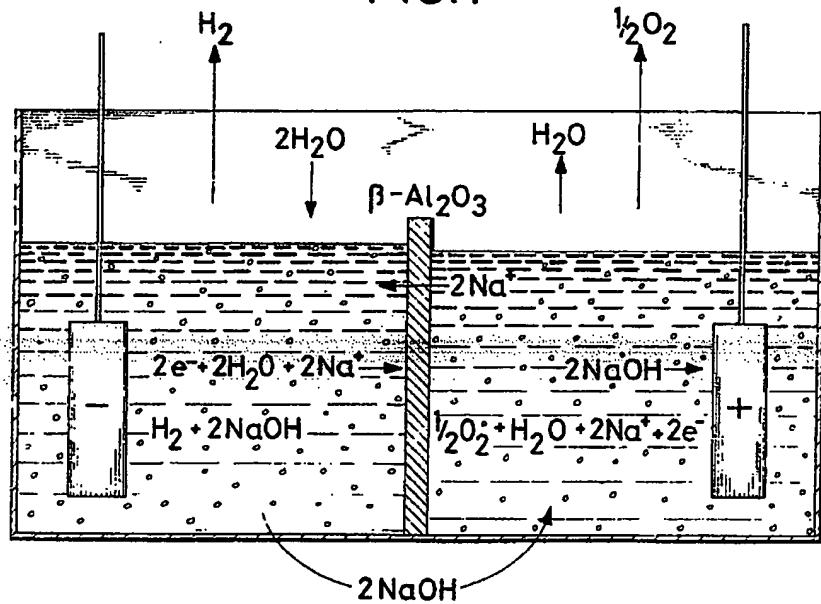


GO 7 2001

1/2

2010333

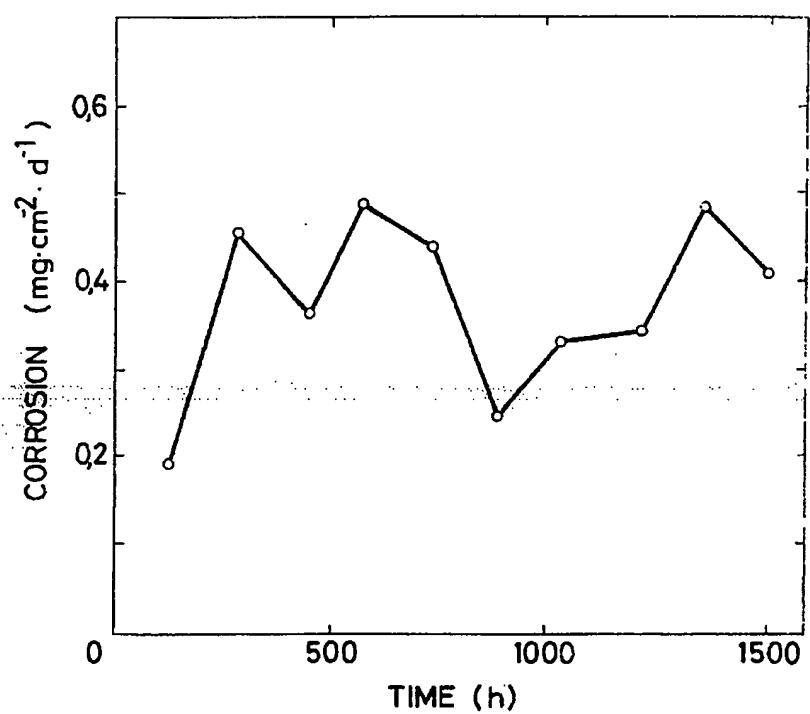
FIG.1



2/2

2010333

FIG. 2



**SPECIFICATION****Process and Apparatus for the Production of Hydrogen and Oxygen**

The invention relates to a process for the 5 production of hydrogen and oxygen by electrolytic decomposition of water in an electrolytic cell containing a molten electrolyte which contains alkali metal ions and has a high OH<sup>-</sup> ion activity, wherein hydrogen and oxygen are separately 10 withdrawn, and to an apparatus for carrying out this process.

Increased attention is being devoted to the 15 production of hydrogen because hydrogen will probably acquire great economic importance as a future energy vehicle. Moreover, where thermal energy must be supplied for this purpose, solar energy and the energy produced in nuclear reactors can be utilised.

The prior art includes a number of processes 20 for the production of hydrogen from water, most of which, however, will not go beyond the experimental stage.

The only hitherto-known process which has 25 been applied on an industrial scale is one in which hydrogen and oxygen are produced by electrolysis using as electrolyte an aqueous solution of potassium hydroxide in a proportion of about 25% by weight. The process is carried out at a 30 temperature between 70 and 90°C. In this process, steel is used as the material for the necessary electrolytic cell and for the cathode, and nickel-coated iron is used for the anode. However, this known process has the disadvantage that the energy consumption is very 35 high. With a current density between 100 and 200 mA/cm<sup>2</sup>, the average energy consumption is 4.6 kWh/Nm<sup>3</sup> of H<sub>2</sub> and in the most favourable case 4.2 kWh/Nm<sup>3</sup> of H<sub>2</sub> (see A. Schmidt "Angewandte Elektrochemie [Applied 40 Electrochemistry]", Verlag Chemie, Weinheim, 1976, page 126).

Endeavours have already been made to lower 45 the energy consumption in the production of hydrogen by carrying out the electrolysis under elevated pressure, although the decomposition voltage increases with increasing gas pressure. However, an advantage of this is that the increase in the voltage is cancelled out because the gas bubbles formed in the electrolyte occupy a 50 substantially smaller volume owing to pressure increase, so that the electrolyte resistance and hence the cell voltage decreases (see A. Schmidt "Angewandte Elektrochemie", Verlag Chemie, Weinheim, 1976, page 127). Nevertheless, there 55 is the disadvantage that the cost of the apparatus employed for the electrolysis is thereby considerably increased.

The prior art also includes a process in which 60 pure water is decomposed with the use of a solid electrolyte. In this case, there is employed as the electrolyte sulphonated polytetrafluoroethylene which is known by the abbreviation PTFE (see L. J. Nutall, A. P. Fickett, W. A. Titterington, "Hydrogen Generation by Solid Polymer

65 Electrolyte Water Electrolysis", Proc. Energy Conf. Miami, 1974, page 9—33 to page 9—37). It is true that this process has the advantage that it is unnecessary to use a diaphragm for separating hydrogen and oxygen, as was considered 70 desirable in the process known until then. It also has the advantage that pure water can be employed, so that corrosive influences are eliminated. However, a considerable disadvantage of this known process resides in the fact that 75 platinum must be used as the electrode material, which substantially precludes application on an Industrial scale.

Owing to the unsatisfactory results of the hitherto-known processes for the production of 80 hydrogen and oxygen, it has also already been proposed, as a reversal of the procedure in H<sub>2</sub>-O<sub>2</sub> fuel cells, to produce hydrogen and oxygen with the use of a 25% potassium hydroxide solution at a working temperature of 80°C. In this 85 case, an electrode made from hot-pressed carbonyl nickel, produced by decomposition of nickel carbonyl, was used as the highly porous cathode.

The two electrolysis chambers necessary for 90 carrying out the electrolysis were separated by an asbestos paper diaphragm (H. Ewe, "Chemie-Ingenieur-Technik", MS 322/76). For improving this process, it has also already been proposed to make the cathode and in addition the anode of 95 Raney nickel, in order thereby to achieve activation. Consequently, the cell voltage was reduced by 20%. However, a disadvantage of this is that the production of Raney nickel electrodes is very costly. Apart from this, the expenditure of 100 energy necessary for carrying out this process is still high.

The proposals for obtaining hydrogen and oxygen in the most economical manner possible also include a process in which the energy

105 liberated by a high-temperature reactor is utilised for the production of a water vapour phase with a temperature of about 1000°C and the water vapour is split by means of a solid electrolyte. The material employed for the electrolyte is ZrO<sub>2</sub> (see

110 W. Dörritz "Chemie-Ingenieur-Technik", MS 323/76, and W. Baukal, M. Dörritz, W. Kuhn "Chemie-Ingenieur-Technik", 48th year, 1976, No. 2, page 132). This process has the advantage that considerable thermodynamic and kinetic 115 advantages are obtained from the use of a solid electrolyte: the stabilised ZrO<sub>2</sub> used as electrolyte in this process is at the same time a conductor of oxygen ions. The electrolyte which is in contact with porous electrodes on both sides

120 simultaneously separates the two gas chambers from one another. However, a disadvantage resides in the fact that, for carrying out the process, the water vapour must be brought to a temperature of at least 900°C, at which the solid electrolyte has sufficient electrical conductivity. Therefore, only at temperatures above 900°C does an electrolytic decomposition take place. Owing to these high temperatures which are 125 necessary for carrying out this process, the

possibility of application on an industrial scale is not yet apparent, or is in any case possible only to a limited extent.

The object of the invention is to provide a process, and apparatus for carrying out the process, by means of which it is made possible to obtain hydrogen and oxygen under economical conditions, so that the process can be applied on a large industrial scale. A particular aim is to 10 reduce the necessary consumption of electrical energy as compared with the hitherto-known processes.

A method suitable in principle for achieving this object is an electrolytic decomposition of 15 water which is passed as vapour into a melt containing  $\text{OH}^-$ , in particular into a melt containing alkali metal ions, as is already described in U.S. Patent Specification 1,543,357. However, the conditions indicated in this U.S. 20 patent specification do not result in industrially useful production of hydrogen, and in particular the indicated separation of the anode chamber and cathode chamber by bells or a greater or lesser spatial distance does not permit a strict 25 suppression of the diffusion of gases so that economic losses, which are no longer tolerable nowadays, are incurred by back-diffusion of gas. The considerable spatial separation, which is necessary in the known process, between the 30 cathode and the anode has the consequence that unduly high voltage drops arise within the cell, and these virtually cancel out the competitiveness of the process. Moreover, the current efficiency is greatly reduced if peroxide compounds formed at 35 the anode can pass without hindrance to the cathode, as is readily possible in the case of the U.S. patent specification. The resulting reductions in yield by about 10% are no longer acceptable economically.

40 A strict separation of the anode chamber from the cathode chamber should provide a remedy for this, but it is very difficult to find separators which are durable and can be used in the hot alkali melt. On the laboratory scale, corundum diaphragms 45 are known, but these are completely unsuitable for undustrial use on a relatively large scale since, on the one hand, they cause a very high resistance in the electrolytic cell, and, on the other hand, large-area separators are extremely difficult 50 to manufacture.

It has now been found that an industrially satisfactory electrolytic decomposition of water in an electrolytic cell, containing a molten electrolyte, can be achieved in an elegant manner 55 when the anode chamber is separated from the cathode chamber by a separator consisting of an aluminium oxide modification which is known as  $\beta\text{-Al}_2\text{O}_3$  and is an ionic conductor.

According to one aspect of this invention there 60 is provided a process for the production of hydrogen and oxygen by electrolytic decomposition of water in an electrolytic cell containing a molten electrolyte which contains alkali metal ions and has a substantial  $\text{OH}^-$  ion activity, wherein hydrogen and oxygen are

separately withdrawn, characterised in that the anode chamber is separated from the cathode chamber by a separator consisting of an aluminium oxide modification which is known as

70  $\beta\text{-Al}_2\text{O}_3$  and is an ionic conductor.

Embodiments of this process can achieve a considerable reduction in the consumption of electrical energy as compared with the hitherto-known processes. In addition, embodiments of

75 the process are suitable for performance at temperatures which render possible a supply of thermal energy in a relatively simple manner. The process can be carried out using materials for carrying out the reactions, such that there is no undue danger to the environment.

In a second aspect the invention provides an electrolytic cell for carrying out the process, having a nickel anode, nickel or graphite cathode.

The invention will be further explained with 80 reference to the attached drawings in which, in particular:

Figure 1 is a diagrammatic representation of an electrolytic cell, illustrating the mode of action of the decomposition of water according to the

90 invention, and

Figure 2 shows graphically the decrease in weight of a  $\beta\text{-Al}_2\text{O}_3$  separator under operating conditions.

It can be seen from Figure 1 that the  $\beta\text{-Al}_2\text{O}_3$  95 diaphragm merely allows alkali metal ions to pass through, whilst oxygen and hydrogen remain separate in the particular electrode chambers and can be withdrawn separately from the latter. To satisfy the mass balance, electrolyte is transferred 100 from the cathode chamber into the anode chamber, and this can be effected in such a way that a carry-over of gases is impossible.

In addition to the advantage already mentioned that a complete separation of the gases is

105 achieved, the separation, according to the invention, of the anode chamber from the cathode chamber by means of a  $\beta\text{-Al}_2\text{O}_3$  separator has the advantage that the total cell voltage can be reduced since, according to the invention,

110 electrode spacings are possible which merely correspond to the wall thickness of the separator, that is to say they can amount to about 1 to 3 mm in practice. The electrical resistivity can here be even lower than that of the melt.

115 Moreover, virtually 100% current efficiency is achieved according to the invention since a transfer of peroxide compounds formed at the anode into the cathode chamber is suppressed.

The electrolysis according to the invention is 120 preferably carried out at temperatures of 300 to 600°C.

Suitable electrolytes are salts or salt mixtures 125 which have a  $\text{OH}^-$  ion activity corresponding to an alkali metal hydroxide content of at least about 5% by weight and the melting point of which is below 800°C, in particular in the range from 300 to 600°C. Preferably, at least one of the salts is represented by an alkali metal hydroxide which, in particular, can be sodium hydroxide. Thus, sodium hydroxide alone or mixtures of sodium hydroxide

130

with other alkali metal hydroxides and/or alkali metal salts, in particular sodium salts, such as fluorides, sulphates or carbonates, are particularly suitable. The addition of lithium hydroxide which reduces the water content of the product gas and has an inhibitory action on the formation of peroxide is particularly advantageous. Potassium hydroxide appears to be less suitable.

A somewhat hygroscopic character of the electrolyte has the advantage that the release of undecomposed water vapour together with the product gases is reduced. Preferably, the electrolyte should thus contain a compound which is hygroscopic under the operating conditions.

The normal water content of the electrolyte melt will be in the region of about 0.5 to 4% by weight.

The  $\beta\text{-Al}_2\text{O}_3$  separator provided according to the invention has a surprisingly high stability in melts of the abovementioned type, and it was possible to demonstrate this by corrosion tests extending over a prolonged period. The result is shown in Figure 2, which is a plot of corrosion in mg.  $\text{cm}^{-2}$  day $^{-1}$  against operating time in hours. From this it can be seen that only a very slight corrosive consumption of the separator takes place, and this is virtually constant in time. The data were recorded in respect of operation at 410°C in molten sodium hydroxide containing 0.5% by weight of water.

A high  $\text{OH}^-$  ion activity of the electrolyte and the relatively high temperature at which the process is carried out are advantageous. In that electrochemical splitting of the water vapour is greatly favoured both thermodynamically and kinetically under these conditions. It may be desirable for the water vapour passed through or into the melt to be under a pressure above normal ambient pressure.

Nickel is very suitable as the material for the cathode and anode. It can, however, also be advantageous to use graphite as the material for the cathode and to use nickel as the material for the anode.

For supplying the water vapour in a particularly advantageous manner, the cathode may be constructed as a hollow body through which the water vapour is supplied.

The current density may be improved by making the cathode or the cathode and anode porous.

According to a preferred embodiment of the invention, porous electrodes can be brought into direct contact with the mutually opposite surfaces of the separator.

If sodium hydroxide is used as the salt melt, it has been found desirable to use nickel or nickel-coated iron as the material for the cell provided to receive the electrolyte.

#### Example 1

Water vapour under normal pressure was electrolysed in a NaOH melt at 430°C. The water vapour was introduced into the melt through a

porous graphite electrode which contained interstitial powdered activated charcoal (obtained by drawing a suspension of activated charcoal through under suction and subsequent drying). A nickel gauze was used as the anode. For separating  $\text{H}_2$  and  $\text{O}_2$ , a ceramic diaphragm consisting of a solid  $\beta\text{-Al}_2\text{O}_3$  electrolyte was provided. The partition had a resistivity of about 0.1  $\Omega \text{ cm}$  at the operating temperature. This value is virtually negligible as compared with the electrical resistivity of the NaOH melt of about 0.45  $\Omega \text{ cm}$ . This was confirmed by an additional measurement which was made.

An  $\alpha\text{-Al}_2\text{O}_3$  crucible was used as the electrolytic cell. Alternatively, a nickel crucible may be employed. Hydrogen was evolved at the cathode, and oxygen was anodically formed. The nickel anode had become covered with a protective layer of nickel oxide; the corrosion of the anode was negligible during the experimental period, and a zero value was measured in practice.

For the removal of moisture, the NaOH melt had been dried before the electrolysis by passing argon (99.99%) through for three hours. The measured residual current density which corresponds to the residual moisture has a value of 10 mA/cm $^2$  at a cell voltage of 1250 mV and a value of 25 mA/cm $^2$  at a cell voltage of 1400 mV. After the introduction of water vapour, the measured current density had a value of 200 mA/cm $^2$  at a cell voltage of 1200 mV and reached a value of 400 mA/cm $^2$  at a cell voltage of 1400 mV. The decomposition potential of NaOH at the operating temperature of 430°C is 2.272 V.

**100 Example 2**  
 Water vapour under normal pressure was electrolysed in a NaOH melt at 400°C. Sheet nickel was employed as the electrode material both for the anode and for the cathode. The water vapour was introduced into the melt through a separate vapour duct in the neighbourhood of the cathode. The amounts of hydrogen and oxygen produced by the electrolysis were analysed by gas chromatography and the current efficiencies were calculated from these values. During the electrolysis which was initially carried out without separation of the two electrode chambers, the current efficiency was 90% of theory. Subsequently, an electrolysis was carried out under the same conditions with the same cell geometry, but with the electrode chambers separated by a  $\beta\text{-Al}_2\text{O}_3$  separator. The current efficiency measured as before now reached 98 to 99% of theory.

**120** A molar ratio, depending on the current density, of 20:1 ( $\text{H}_2\text{O}:\text{H}_2$ ) was measured at 400 mA/cm $^2$  in the product gas from the electrolytic cell.

#### Example 3

Water vapour under normal pressure was electrolysed in a hydroxide melt of the composition NaOH:LiOH=1:1. The construction

and dimensions of the cell were not changed from those of Example 2. A molar ratio of  $H_2O:H_2$  of 8:1 at a current density of 400 mA/cm<sup>2</sup> was measured in the product gas from the electrolytic cell. This means that the water content of the product gas was markedly reduced under the conditions of this example.

The current efficiency measured as in Example 2 was in this case virtually 100% of theory, that is 10 to say it was yet further improved. To enable the improvement in current efficiency, which can be achieved by modifying the electrolyte, to be demonstrated even more clearly, the current efficiency was determined without a separator 15 (under the same conditions). In this case, the efficiency was 96% as compared with 90% (which was obtained under the same conditions but using the electrolyte of Example 2). In this latter case, that is to say without the use of the 20 separator, the separation of gas had of course deteriorated.

#### Claims

1. Process for the production of hydrogen and oxygen by electrolytic decomposition of water in 25 an electrolytic cell containing a molten electrolyte which contains alkali metal ions and has a high  $OH^-$  ion activity, wherein hydrogen and oxygen are separately withdrawn, characterised in that the anode chamber is separated from the cathode 30 chamber by a separator consisting of an aluminium oxide modification which is known as  $\beta$ - $Al_2O_3$  and is an ionic conductor.
2. Process according to claim 1, characterised in that the electrolyte contains a compound which 35 is hygroscopic at the operating temperature.
3. Process according to claim 1 or claim 2, characterised in that the electrolyte contains a compound which is hygroscopic at the operating temperature.
- 40 4. Process according to any one of the preceding claims, characterised in that an alkali metal hydroxide or an alkali metal hydroxide

mixture, if desired together with alkali metal salts, is used as electrolyte.

- 45 5. Process according to claim 4 characterised in that sodium hydroxide is used as the alkali metal hydroxide.
6. Process according to claim 5 characterised in that a mixture of lithium hydroxide and sodium 50 hydroxide is used as electrolyte.
7. Process according to any one of the preceding claims characterised in that water vapour is passed through or into the melt under a pressure above ambient pressure.
- 55 8. Process for the production of hydrogen and oxygen according to claim, substantially as described herein.
9. Electrolytic cell for carrying out the process of any one of the preceding claims, having a 60 nickel anode, a nickel or graphite cathode, a  $\beta$ - $Al_2O_3$  separator separating the anode chamber of the cell from the cathode chamber, means for supplying water vapour to the electrolyte and means for separately withdrawing hydrogen and 65 oxygen from the cathode chamber and anode chamber respectively.
10. Electrolytic cell according to claim 9, characterised in that the cathode is constructed as a hollow body for the supply therethrough of 70 water vapour to the electrolyte.
11. Electrolytic cell according to claim 9 or claim 10 characterised in that either the cathode or both the anode and the cathode are porous.
12. Electrolytic cell according to any one of 75 claims 9 to 11 wherein the electrodes are in contact with respective opposite faces of the separator.
13. Electrolytic cell according to any one of claims 9 to 12, characterised by a receiver vessel 80 for the electrolyte, which vessel consists of nickel, nickel-coated iron or  $\alpha$ -alumina.
14. Electrolytic cell according to claim 9 and substantially as herein described with reference to the drawings.